Pair Distribution Function for Nanoparticle Studies

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Composed of only a few thousand atoms, a nanoparticle can have unique optical, electronic, magnetic, or chemical properties. Such properties are enabling new types of biosensors, drug delivery methods, lubricants, and solar cells and are intimately related to the nanoparticles' structures. However, the preferred tools for measuring the structures of bulk materials—conventional diffraction methods with x-rays or neutrons—often give poor-quality information when applied to nanoparticles. Using the pair distribution function (PDF) method to analyze neutron-diffraction data obtained with the neutron powder diffractometer, we have obtained high-quality structural measurements of gold nanoparticles. These measurements can be used to validate atom-level computer models of nanoparticles and to characterize their structures.

The obvious difference between nanoparticles and their bulk counterparts is size. Because of the nanoparticles' tiny size, conventional diffraction methods often fail to yield accurate measurements of their structure. Those methods assume an infinitely periodic system, which does not work with nanosizes. By contrast, the pair distribution function has no periodicity requirement and thus no limitation on particle size.

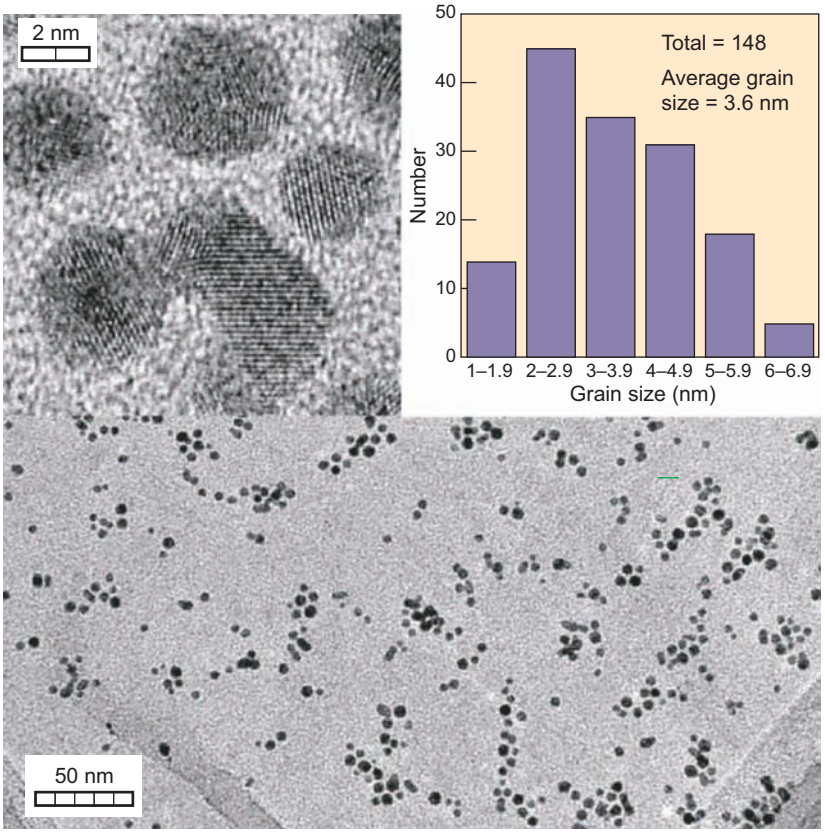

Figure 1. Transmission Electron Micrograph (TEM) of Gold Particles
Individual gold nanoparticles are shown in this TEM. The inset is a high-resolution TEM of a few nanoparticles. (b) The histogram shows the particle size distribution. The nanoparticles' mean diameter is ~3.6 nm.

Another difference is that the number of atoms on the surface of a bulk material is small compared with the number of atoms in the core. By contrast, a nanoparticle's surface atoms can comprise up to 20 percent of its atoms. Again, since the PDF does not require periodicity, it is an ideal method for studying differences

between the surface and core structures of a nanoparticle.

To demonstrate the PDF's ability to measure nanoparticle structure, we took diffraction data with the neutron powder diffractometer (NPDF) on flurothiol-capped gold nanoparticles and on a bulk gold sample. We then Fourier-transformed the diffraction data to obtain the PDFs. Figure 1 shows a transmission electron micrograph (TEM) of the individual gold nanoparticles and a histogram of the particle size distribution; the average size is about 3.6 nanometers. Neutron-scattering experiments usually require large samples; this experiment required 1.5 grams of nanoparticles. The measurement lasted for about 15 hours.

Figure 2 shows the experimental PDFs for bulk gold (a) and gold nanoparticles (b). The PDF for bulk gold decreases with r, the atom–atom separation distance, because of the NPDF's finite resolution. However, atom–atom correlations (the small peaks) are clearly visible for large values of r. By contrast, the PDF peaks for the nanoparticles diminish at much smaller r values because there are no atom–atom pairs separated by more than the particle diameter (the vertical dashed line in Figure 2). Because we determined the PDF to atom–atom distances of 10 nanometers—much larger than the nanoparticles' diameters—the PDF provides all atom–atom separation distances of the nanoparticles.

Figure 3 shows the PDFs from experimental data for gold nanoparticles at two temperatures. The peaks at ~0.28 nanometer correspond to the closest distance between the gold atoms and confirm previous findings that gold nanoparticles have slightly smaller unit cells than bulk samples do. The sharpness and symmetry of the peaks also show that there is no significant relaxation of the structure near the nanoparticle's surface. The

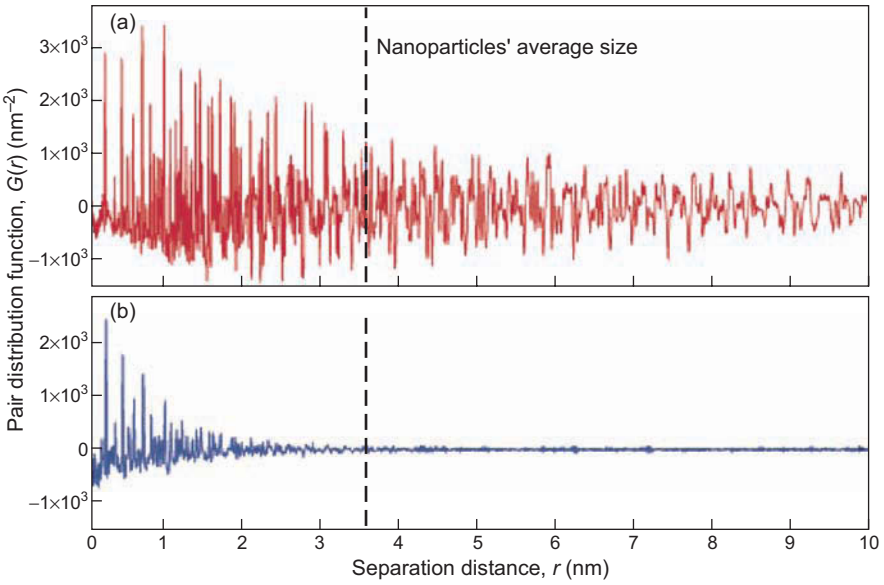

Figure 2. PDFs of Bulk and Nanoparticle Gold Samples
The PDFs of a bulk gold sample and a nanoparticle gold sample to an atom–atom distance (r) of 10 nm are shown in (a) and (b), respectively. The data were taken with NPDF spectrometer at LANSCE. The dashed line marks the nanoparticles' average size. The bulk sample shows atom–atom correlations over the full range of atom–atom separation distances. The PDF peaks decrease with r because of the NPDF's finite resolution. By contrast, there are PDF peaks for the nanoparticle sample only out to the nanoparticles' mean diameter.

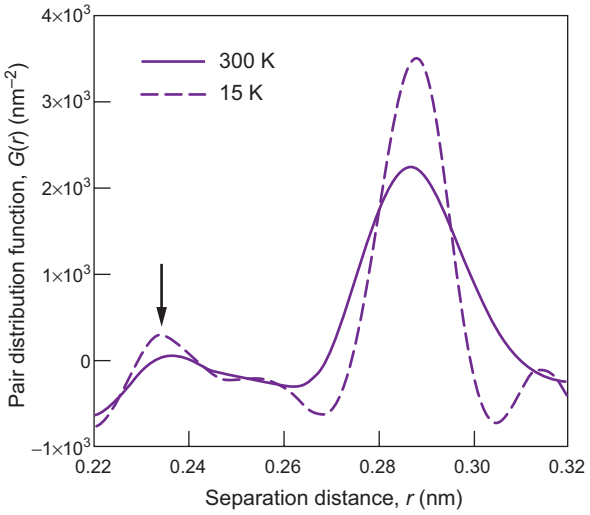

Figure 3. PDFs for Gold Nanoparticles as a Function of Temperature
The PDFs [$G(r)$] at small atom–atom separation distances (r) for experimental data are shown for two temperatures. The small peaks indicate the distance between surface gold atoms and the sulphur atoms in the nanoparticle coating. The large peaks indicate the nearest-neighbor distance between the gold nanoparticles.

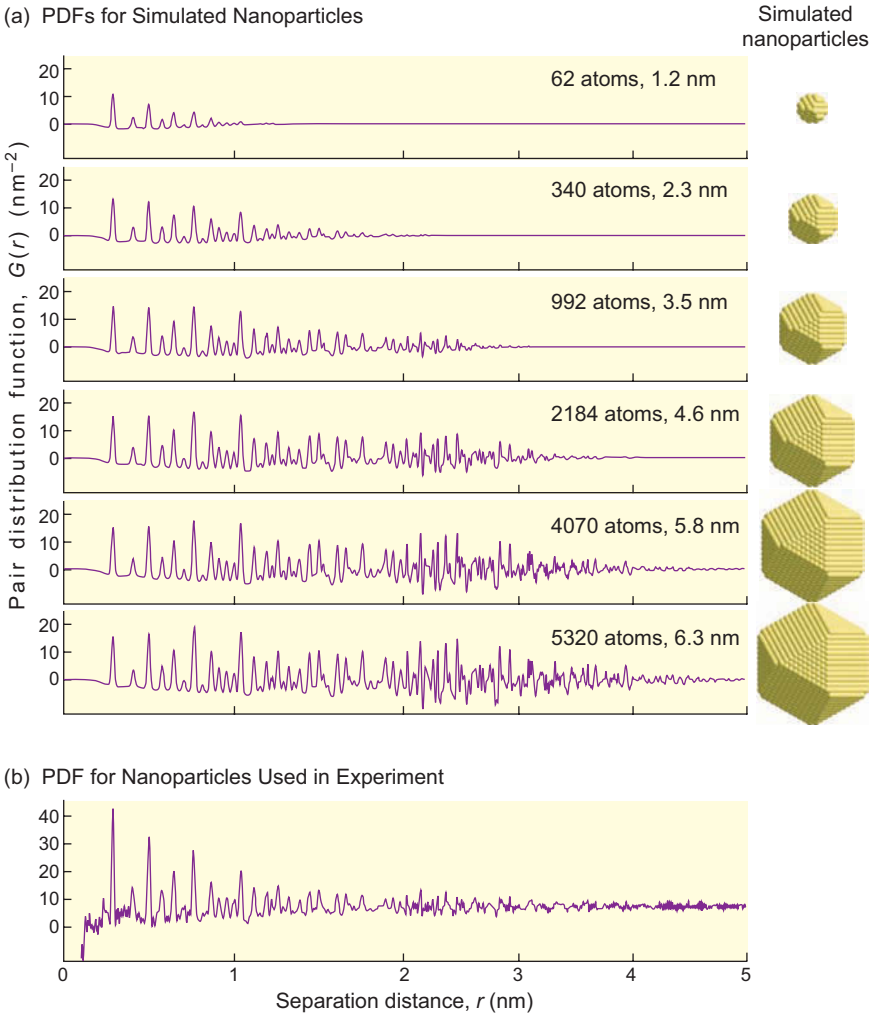

Figure 4. PDFs Calculated for Simulated and Real Gold Nanoparticles
(a) Shown here are PDFs for simulated cuboctahedral gold nanoparticles whose sizes are between 1.2 and 6.3 nm. (b) This PDF of gold nanoparticles was calculated from experimental data and is also shown in Figure 2(b). The data were obtained with the NPDF spectrometer.

arrow corresponds to the closest distance between the surface gold atoms and the sulfur atoms in the thiol capping the nanoparticles. This peak is sharper at lower temperatures because thermal vibrations are reduced.

The next step in these studies will be to refine the experimental PDFs with a structural model. One usually starts refining a model based on the lattice parameters and the positions of the atoms in the bulk material (gold, in this case). The refinement yields structural parameters, which are then compared with the results from the bulk material. In many cases, the PDF contains evidence of disorders (for example, structural distortions at the nanoparticles' surfaces, which contain significant fractions of the atoms in the nanoparticles' structures). These deviations from the average structure are hidden to the Rietveld analysis, and describing them requires modifications to the atomic model. A detailed discussion of what is involved is beyond the scope of this article, but the interested reader can refer to Page et al. (2004).

Although the experiments used to obtain PDFs are usually quite straightforward, it is often fairly difficult to do computer simulations at the atomic level and compare them with the experimental data. A bulk specimen will contain about 10^{23} atoms or more—well beyond the simulation capabilities of state-of-the-art computers. But since a typical nanoparticle might contain only a few thousand atoms, a complete nanoparticle can be modeled on a computer. Figure 4 shows the PDFs obtained with computer models for cuboctahedral gold nanoparticles of different sizes. High-quality experimental PDFs obtained with instruments such as the NPDF can be used to validate computer simulations of nanoparticles. The PDF method in general and especially as applied to nanoparticles will continue to play a significant role in advancing our knowledge of complex materials.

Further Reading

Egami, T., and S. J. L. Billinge. 2003. *Underneath the Bragg-Peaks: Structural Analysis of Complex Materials*. Amsterdam; Boston: Pergamon.

Page, K. L., Th. Proffen, H. Terrones, M. Terrones, L. Lee, Y. Yang, et al. 2004. Direct Observation of the Structure of Gold Nanoparticles by Total Scattering Powder Neutron Diffraction. *Chem. Phys. Lett.* **393** (4–6): 385